

# PATENT SPECIFICATION

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 (72) Inventor JOHN BREWSTER ROSE



(72) Inventor JOHN BREWSTER ROSE

(54) BISPHENOL DERIVATIVE

(71) We, IMPERIAL CHEMICAL INDUSTRIES LIMITED, Imperial Chemical House, Millbank, London SW1P 3JF, a British Company, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

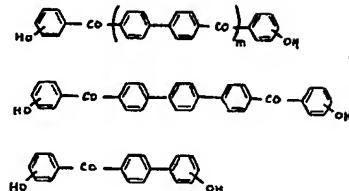
This invention relates to aromatic polymers and a bisphenol derivative which of particular use in the manufacture of aromatic polymers containing ketone linking groups.

15 According to the present invention we provide a hydrated dipotassium salt of bis-(4-hydroxyphenyl) ketone.

This salt is conveniently made by the reaction of potassium hydroxide with bis-(4-hydroxyphenyl) ketone. Thus the bisphenol may be stirred in a potassium hydroxide solution, in the ratio of 1 mole of bisphenol to two moles of hydroxide, until the bisphenol has dissolved, and then the water evaporated off e.g. by spray drying, to give the hydrated potassium salt.

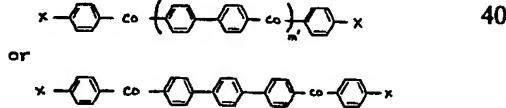
25 The bisphenate is of particular use as one of the condensants in the process described in our U.K. application 25202/73 (Serial No. 1,414,421) wherein a monomer mixture comprising

30 (1) 49 to 50% molar of at least one di(alkali metal) salt of a bisphenol of formula

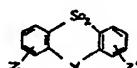


at least 95% of the phenolic OH groups being in the *para* position, and

(2) 51 to 50% molar of at least one dihalo compound of formula



where X is F, Cl or Br, each of m and m' is zero, 1, 2 or 3, and some of the ketone groups may be replaced by sulphone groups provided that the proportion of sulphone groups (if present) to ketone groups in the monomer mixture is not greater than 25 mole % and the molar percentages of monomers in the mixture sum to 100%, is heated at temperatures of 250°C to 400°C (preferably at 280°C to 350°C) in the presence of an aromatic sulphone having the formula



in which Y is a direct link, an oxygen atom or two hydrogen atoms (one attached to each benzene ring) and Z and Z' are selected from hydrogen atoms and phenyl groups and may be the same or different, so as to produce an aromatic polymer having reduced viscosity of between 0.8 and 3.0, preferably between 1.0 and 2.0 [as measured 5 at 25°C on a solution of polymer in concentrated sulphuric acid (density 1.84 g/cm<sup>3</sup>) containing 1 g of polymer in 100 cm<sup>3</sup> of solution] whose molecular chains comprise 1,4-phenylene groups, oxygen atoms and ketone groups and optionally one or more 4,4'-bi-10 phenylene, terphenylene and/or sulphone groups.

The preferred aromatic sulphone is diphenyl sulphone (i.e. Y, Z and Z' are all hydrogen atoms).

The polymerisation reaction should be carried out under substantially anhydrous conditions. The most likely source of water is from the hydrated salt and so, before use in 25 the polymerisation reaction it should therefore be dehydrated. We have found that this may conveniently be performed by heating the hydrated salt in the presence of the aromatic sulphone used in the polymerisation process.

Accordingly we also provide a method of dehydrating a hydrated dipotassium salt of bis-(4-hydroxyphenyl) ketone comprising heating the hydrated salt in the presence of 30 an aromatic sulphone of formula



in which Y is a direct link, an oxygen atom or two hydrogen atoms (one attached to each benzene ring) and Z and Z' are selected from 35 hydrogen atoms and phenyl groups and may be the same or different, at a temperature above 150°C, preferably above 200°C and preferably under partial vacuum, e.g. 25 to 400 torr. A particular advantage in dehydration of the di(alkali metal) salt in the presence of the aromatic sulphone in the polymerisation vessel is that there is no splashing of the salt on the walls of the reaction vessel and hence stoichiometry of the polymerisation reaction is maintained because the aromatic 45 sulphone does not boil. The dihalo monomers can then be added after evolution of water (as evident for example by foaming) has 50 ceased and temperature subsequently increased to the polymerisation temperature. The polymerisation is also preferably carried out in an inert atmosphere e.g. argon or nitrogen. The reaction vessel can be made from glass 55 but is preferably made from stainless steels,

other than those which undergo surface crazing at the reaction temperatures in the presence of alkali metal halide, or vessels made of or lined with titanium or nickel or an alloy thereof or some similarly inert material.

The polymerisation reaction is carried out at temperatures between 250°C and 400°C, preferably between 280°C and 350°C. As with all chemical reactions, an increase in reaction temperature leads to shorter reaction times but with attendant risk of product decomposition whereas reduction in reaction temperature leads to longer reaction times but less product decomposition. However a temperature should be used which maintains polymeric material in solution. In general the solubility of polymer in the aromatic sulphone increases with temperature and with increasing proportion of sulphone groups in the polymer chain. Accordingly polymers having a higher proportion of sulphone groups can if desired be produced at slightly lower polymerisation reaction temperatures.

In order to obtain products of decreased absorbance, it may be advantageous to use a prepolymerisation heating stage in which monomers are heated together at 200°C to 250°C preferably 220°C to 245°C.

To neutralise any reactive oxygen-containing anions a reagent therefor may be introduced at the termination of the polymerisation reaction. Reactive monofunctional halides, for example methyl chloride and reactive aromatic halides number for example bis-(4-chlorophenyl) sulphone and 1-benzenesulphonyl-4-chlorobenzene are particularly suitable. The reaction mixture may be (i) allowed to cool and solidify, (ii) ground, (iii) extracted with a solvent for the diaryl sulphone, conveniently with alcohol (e.g. methanol) or acetone, and water, and finally (iv) dried.

The dipotassium salt of bis-(4-hydroxyphenyl) ketone is only slightly soluble in the aromatic sulphone used in the polymerisation process. Slight solubility of the said potassium bisphenate in the aromatic sulphone is important; it must dissolve sufficiently to undergo the polycondensation reaction but must remain at a low concentration in the polymerisation reaction solution so as to reduce the risk of the ketone link being attacked by the nucleophile. Whilst the above procedure leads to increased reaction times over those exemplified in British patent specifications 1,078,234 and 1,177,183, the resulting polymer has improved linearity and higher molecular weight and exhibits increased toughness.

The advantage gained by use of a solvent in which the said dipotassium bisphenate is only slightly soluble is wholly unexpected in view of a paper by R. N. Johnson, A. G. Farnham, R. A. Clendinning, W. F. Hale and C. N. Merriam in *Journal of Polymer Science* 1967, Vol. 5, Part A-1, pages 2375

to 2398, which at pages 2378 to 2380 teaches that in polycondensation of a di(alkali metal) bisphenate with a dihalobenzoid compound, the use of a dipolar aprotic solvent in which both polymer and said di(alkali metal) salt have highest solubility leads to polymers having highest molecular weight. The authors of this paper therefore preferred dimethyl sulphoxide, dimethyl sulphone and 1,1-dioxothiolan (sulpholane) and showed that the polymers prepared therein have higher molecular weight than those prepared in diphenyl sulphone. 5

It has been found surprisingly that polymer provided by the above polymerisation process in the aromatic sulphone has higher molecular weight, and hence films therefrom have greater toughness, than polymers similarly prepared but using the preferred solvents of the above 10 authors, two of whom (Johnson and Farnham) are named as inventors in respect of British specification 1,078,234 and a third (Clendinning) is named as inventor in respect of British specification 1,177,183.

20 For use in the above polymerisation process, the dipotassium salt should be in a finely divided form having particle size less than 1 mm, preferably less than 500  $\mu\text{m}$ .

The invention is illustrated by the following Examples. Reduced viscosities were measured at 25°C in a solution of polymer in concentrated sulphuric acid (density 1.84 g/cm<sup>3</sup>) containing 1 g of polymer in 100 cm<sup>3</sup> of solution. Absorbance was measured at a wavelength of 550 nm in a 10 mm cell using a solution of polymer in concentrated sulphuric acid as used for reduced viscosity.

EXAMPLE 1.

Bis-(4-hydroxyphenyl) ketone (428.4 g; 2.00 mole) was washed (using water) into a polyethylene vessel containing 4 dm<sup>3</sup> of 1 M aqueous potassium hydroxide. The mixture was stirred until all the ketone had dissolved and the solution was stored under nitrogen.

45 A sample (320 g) of the solution was evaporated to dryness in a glass flask to leave the solid hydrated dipotassium salt. This hydrated salt was finely ground. A portion of the hydrated salt was dissolved in water and analysed by titration potentiometrically against 0.1 M sulphuric acid. It was found to contain 89.08% molar of the dipotassium salt of bis-(4-hydroxyphenyl) ketone.

55 A sample of the above finely ground hydrated dipotassium salt (91.0318 g; 0.2792 mole) was charged together with recrystallised diphenyl sulphone (150 g) to a glass flask (capacity 1 dm<sup>3</sup>) fitted with stirrer, thermocouple probe, nitrogen purge and an air condenser. The flask was flushed with nitrogen and heated on a solder bath at 230°C in order to dehydrate the dipotassium salt. After one minute, the pressure in the flask was reduced to 60 torr; after a further 15 minutes at 230°C, stirring was commenced and continued for a further 15 minutes. Water distilled from the resulting yellow slurry. The apparatus was filled with nitrogen and pressure therein increased to atmospheric. Bis-(4-chlorophenyl) ketone (70.6403 g; 0.2813 mole, recrystallised) and diphenyl sulphone (19 g; recrystallised) were added to the slurry. The slurry was heated under nitrogen with stirring at 230°C for 16 hours and then polymerised at 330°C for 6 hours. After six hours, crystallised bis-(4-chlorophenyl) sulphone (20 g) was added as end-stop. The reaction mixture was cooled to room temperature, crushed and milled and then boiled twice with acetone, boiled with water (containing 1% volume/volume glacial acetic acid), boiled with water and extracted with acetone/methanol (1:1 by volume), each boiling lasted for 5 minutes. The polymer was then dried at 135°C for 3 hours at a pressure of 5 torr. The polymer yield was 100.3 g. 65

The reduced viscosity and absorbance of the polymer were 1.27 and 0.17 respectively. The melt viscosity was 1.14 kNsm<sup>-2</sup> at 400°C using a shear of 100 s<sup>-1</sup> was measured on a ram extruder. A fibre was cold-drawn from the extrudate. 70

A tough film was compression-molded from the polymer at 400°C and placed between two overlapping glass plates. The plates and film were pressed together using a spring clip and heated to 400°C. On cooling to room temperature, the glass broke on attempting to pull the plates apart. In a similar experiment, the glass also broke on attempting to pull the plates apart after immersion of the assembly in acetone for 30 minutes at room temperature. 80

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EXAMPLE 2.

A sample of hydrated dipotassium salt of bis-(4-hydroxyphenyl) ketone, finely ground to pass through a sieve having mesh diameter 500  $\mu\text{m}$ , was estimated by titration against standard solution of sulphuric acid in methanol/water (1:1 volume/volume). Accordingly, a sample (0.07463 mole) of the dipotassium salt was weighed into a glass flask (capacity 250 cm<sup>3</sup>) fitted with stirrer, thermocouple probe, nitrogen purge and an air condenser. Diphenyl sulphone (ground; 40 g; melting point 124 to 125.5°C recrystallised from methanol) was introduced into the flask and powder-blended with the dipotassium salt. The flask was flushed with nitrogen and heated on a solder bath at 230°C. As the diphenyl sulphone melted, the stirrer was started, nitrogen purge at 15 cm<sup>3</sup> per minute commenced and the pressure in the flask reduced slowly to 200 torr. The pressure was reduced slowly over a further 15 minutes to about 30 torr. Water distilled from the mixture and a lemon-

yellow slurry of the dipotassium salt in diphenyl sulphone remained in the flask. Care was taken to ensure that the diphenyl sulphone did not boil and hence did not splash the dipotassium salt onto the upper walls of the flask. The apparatus was then filled with nitrogen and pressure there increased to atmospheric. Bis-(4-chlorophenyl) ketone (11.3004 g; 0.04500 mole; melting point 146.0 to 147.0°C distilled and then recrystallised from methyl ethyl ketone), bis-(4-chlorophenyl) sulphone (8.6153 g; 0.03000 mole, melting point 148.0 to 149.0°C, recrystallised from isopropanol) and recrystallised diphenyl sulphone (15.7 g) were added to the flask. A bubbler was fitted to the air condenser and the solder bath temperature was raised to 290°C. After 30 minutes at 290°C, a cold trap at about -80°C was fitted between the air condenser and the bubbler. The solder bath was maintained at 290°C and the reaction proceeded for 17 hours during which the reaction temperature was close to 290°C, nitrogen purge was maintained at 15 cm<sup>3</sup> per minute and a yellow solution of polymer formed in the flask. After the reaction period, the trap was removed and found to contain 0.1078 g of condensate which was largely water. Methyl chloride was then bubbled through the polymer solution for twenty minutes whereupon the reaction mixture became almost colourless. The reaction mixture was cooled to room temperature, ground, extracted three times with methanol, then with hot water, then with hot acetone/methanol (1:1 by volume) and finally dried. The polymer had a reduced viscosity of 2.57. The solution was pale orange/yellow in colour and free from gelatinous material and had an absorbance of 0.08. The polymer was compression-moulded at 360°C to give a tough opaque film (crystalline) when the mould was allowed to cool to 25°C over 1 hour. When the mould was cooled within two minutes a very tough, clear film (amorphous) resulted.

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5. A method of dehydrating a salt as claimed in any one of Claims 1 to 4 comprising heating the hydrated salt in the presence of an aromatic sulphone of formula

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6. A method as claimed in Claim 5 in which the salt is heated at a temperature above 200°C.

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7. A method as claimed in Claim 5 or Claim 6 in which the salt is heated under a partial vacuum of 25 to 400 torr.

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8. A method as claimed in any of Claims 5 to 7 in which the aromatic sulphone is diphenyl sulphone.

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9. A method as claimed in Claim 5 substantially as hereinbefore described and illustrated with reference to any one of the Examples.

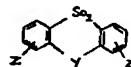
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10. A salt as claimed in Claim 1 having a particle size of less than 1 mm.

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11. A salt as claimed in Claim 2 having a particle size of less than 500 mm.

12. A salt as claimed in Claim 1 substantially as hereinbefore described and illustrated with reference to any one of the Examples.



in which Y is a direct link, an oxygen atom or two hydrogen atoms (one attached to each benzene ring) and Z and Z' are selected from hydrogen atoms and phenyl groups and may be the same or different, at a temperature above 150°C.

13. A salt as claimed in Claim 1 having a particle size of less than 1 mm.

14. A salt as claimed in Claim 2 having a particle size of less than 500 mm.

15. A salt as claimed in Claim 1 substantially as hereinbefore described and illustrated with reference to any one of the Examples.

C. GRATWICK,  
Agent for the Applicants.